

Intramolecularly Sn–N Coordinated Organotin Hydrides

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In recent years, internally Sn–N coordinated organotin hydrides have found an application in organic syntheses, which involve radical chain reactions. Unique reactivity of such hydrides suggests the potential of intramolecular coordination for the control of radical reactions. When the tin hydrides are used in the presence of Lewis acids single-enantiomer outcomes are accessible. This opens a new aspect of free radical chemistry. The intramolecular Sn–N coordination enhances also nucleophilic character of the tin hydrides in reduction of ketones under mild reaction conditions. The occurrence of intramolecular interaction between the nitrogen and tin atoms can be additionally based on the changes in the characteristic values of the ¹H, ¹³C, ¹⁵N and ^{117/119}Sn NMR parameters and their interrelations.

Key words: tin hydrides, radicals, reduction, stereoselection, Sn–N coordination, NMR spectroscopy

Seven Membered Ring Sugars: A Decade Update

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Chemical synthesis of septanoses (seven membered ring sugars) and oligosaccharides containing septanosyl residue, the role of seven membered ring sugars as intermediate compounds, conformation of the septanose ring, and the biological activity of septanoses are discussed. This review covers the literature published from 1995 till 2005.

Key words: septanoses, seven membered ring sugars, synthesis, conformation, biological activity

Synthesis and Ferromagnetic Interaction in Oxamido-Bridged Copper(II)–Chromium(III) Heterotetranuclear Complexes

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Two new μ -oxamido-bridged copper(II)–chromium(III) heterotetranuclear complexes formulated as $[\text{Cu}_3(\text{dmoxae})_3\text{Cr}](\text{ClO}_4)_3$ (**1**) and $[\text{Cu}_3(\text{dmoxpn})_3\text{Cr}](\text{ClO}_4)_3$ (**2**), where dmoxae and dmoxpn represent N,N' -bis[2-(dimethylamino)ethyl]oxamido and N,N' -bis[3-(dimethylamino)propyl]oxamido dianions, respectively, have been synthesized and characterized by the elemental analyses, spectroscopic (IR, UV, ESR) studies, magnetic moments (at room-temperature) and by molar conductivity measurements. It is proposed that these complexes have oxamido-bridged structures consisting of three copper(II) ions and a chromium(III) ion, in which the chromium(III) ion has an octahedral environment and the three copper(II) ions have a square-planar environment. The two heterotetranuclear complexes were further characterized by variable-temperature magnetization (3–300 K) measurements and the magnetic data have been used to deduce the indicated heterotetranuclear structure. The results derived from least-squares fit of the experimental data have confirmed that the operation of a ferromagnetic interaction between the adjacent copper(II) and chromium(III) ions occurs through the oxamido-bridge within each molecule. On the basis of the spin Hamiltonian operator, $\hat{H} = -2J(\hat{S}_{\text{Cu}_1} \cdot \hat{S}_{\text{Cr}} + \hat{S}_{\text{Cu}_2} \cdot \hat{S}_{\text{Cr}} + \hat{S}_{\text{Cu}_3} \cdot \hat{S}_{\text{Cr}})$, the magnetic analyses were carried out for the two copper(II)–chromium(III) heterotetranuclear complexes and the spin-coupling constants (J) were evaluated as $+9.28 \text{ cm}^{-1}$ for (**1**) and $+9.63 \text{ cm}^{-1}$ for (**2**). The influence of the symmetry of the magnetic orbitals on the nature of the magnetic interaction between the paramagnetic centers is preliminary discussed.

Key words: μ -oxamido-bridge, copper(II), chromium(III), heterotetranuclear complexes, ferromagnetic interaction

Synthesis and UV-vis Study of a New Strongly Solvatochromic Merocyanine-like Dye with Modified Donor Part

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The new solvatochromic dye, deprotonated 5-(6-hydroxynaphthyl-2)-7,7-dimethyl-7H-indolo[1,2-a]quinolinium perchlorate, was synthesized and studied in numerous solvents differing in polarity. The interpretation of the obtained results was made on the basis of VBHB model. The comparison with a dye of shorter distance between donor and acceptor parts indicated that the new dye is the best of all known solvatochromic merocyanines, comparable with Reichardt-Dimroth betaine.

Key words: solvatochromic dye, merocyanine, solvatochromic effect, VBHB model

**Esters of *p*-Nitrophenol in Synthesis of 1-*N*-Monoamide
and 1,7-Bis-*N,N'*-amide Derivatives of
1,4,7,10-Tetraazacyclododecane**

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The efficient synthesis of *N*-monoamide and bis-*N,N*-amide-1,4,7,10-tetraazacyclododecanes is reported.

Key words: cyclen, active esters, acylation

Chemoselectivity of the [2+3]-Cycloaddition of Thiocarbonyl Ylides with 5-Benzylidene-3-phenylrhodanine

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Reactions of three different thiocarbonyl *S*-methylides, generated from thiobenzophenone (**2**), 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**3**), and adamantanethione (**8**), respectively, and diazomethane, with 5-benzylidene-3-phenylrhodanine (**12**) were carried out. The aromatic thiocarbonyl ylide **1a** adds chemoselectively to the C,C-double bond, but the spirocyclic 1,3-dithiolane **18**, *i.e.* the [2+3]-cycloadduct with the C=S group of **12**, was also formed as a minor product. In the cases of the aliphatic thiocarbonyl ylides **6** and **20**, the [2+3]-cycloaddition occurred at the exocyclic C,C-double bond exclusively to give the spirocyclic tetrahydrothiophene derivatives **23** and **21**, respectively. A smooth acid-catalyzed decomposition of **18** yielded the 2-diphenylmethylidene derivative **19**. The formation of product **24**, which was obtained in the reaction of the sterically congested ylide **6** with **12**, is explained by a 1,4-H-shift in an intermediate zwitterionic adduct. The structures of the tetrahydrothiophenes **17**, **21** and **23**, as well as that of **24**, were established by X-ray crystallography.

Key words: thiocarbonyl ylides, 1,3-dipolar cycloaddition, rhodanine, 2,5-dihydro-1,3,4-thiadiazoles, crystal structure

Oxidation of Benzylic Alcohols with I_2/K_2CO_3 /*tert*-butanol: Formation of Aldehydes or Dimeric Esters

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Oxidation of a series of aromatic and heteroaromatic benzylic alcohols with molecular iodine in *tert*-butanol in the presence of potassium carbonate has been studied. Oxidation of most benzylic alcohols affords the corresponding aldehydes in reasonable yields. The reaction has been shown to be compatible with amino, formyl, methylthio groups and thiophene ring in the molecule. Oxidation of the electron-poor benzylic alcohols such as nitrobenzyl alcohols and (benzimidazol-2-yl)methanol results in the formation of the corresponding dimeric esters.

Key words: benzylic alcohols, oxidation, molecular iodine, aldehydes, dimeric esters

Characterization, Crystal Structure, and Solution Studies of a Proton Transfer Compound Obtained from 2,6-Pyridinedicarboxylic Acid and 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane

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The proton transfer compound, (DA18C6H₂)(pydcH)₂·0.25H₂O, has been prepared from the reaction between 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, diaza-18-crown-6 (DA18C6), and 2,6-pyridinedicarboxylic acid, dipicolinic acid (pydcH₂). The characterization was performed using ¹H and ¹³C NMR, IR spectroscopy and single crystal X-ray diffraction analysis. The asymmetric unit consists of one (DA18C6H₂)²⁺ cation adopting a sigmoidal conformation which interacts with two (pydcH)⁻ anions *via* hydrogen bonds involving the protonated amine groups of the diazacrown ether. –COOH...⁻OOC– head-to-tail hydrogen bonds generate 2D undulating layers along [100] and [001] in the crystal lattice. The protonation constants of DA18C6 and pydcH₂ and equilibrium constants for the reaction of the two reactants were determined by potentiometric *pH* titration. The solution studies supported the formation also in solution of (DA18C6H₂)(pydcH)₂ as the most abundant species at *pH* = 3.4.

Key words: 2,6-pyridinedicarboxylic acid, diaza-18-crown-6, hydrogen bonds, crystal structure, solution studies

Selective Oxidation and Oxidative Dehydrogenation of Isobutane on Mo-V-Te-P Mixed Metal Oxide Catalysts

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$\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x$ ($x = 0-0.5$) catalysts have been prepared and tested in the selective oxidation of isobutane. Among them, $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_{0.3}$ catalyses the direct oxidation of isobutane to methacrolein and methacrylic acid with 33% selectivity, and a total dehydrogenation (olefin plus methacrolein and methacrylic acid) selectivity up to 63% at 400°C.

Key words: isobutane, isobutylene, selective oxidation, mixed metal oxides catalysts

Hydroxylation of Alkanes Using H₂O₂ or *tert*-BuOOH Catalyzed by Silica-based Fe(III) Interphase Catalysts

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Two novel silica-based *organic-inorganic hybrid* (interphase) Fe(III) catalysts have been successfully prepared by the flexible ligand method, characterized and applied to the efficient catalytic oxidation of various types of substrates using 30% H₂O₂ or *tert*-BuOOH under mild conditions. The catalysts can be recovered and reused for four reaction cycles with total turnover numbers being about 29 using cyclohexene as the substrate. The mechanism for the O–O bond cleavage was proposed based on the results in combination with previous experimental results.

Key words: methane monooxygenase, biomimetic hydroxylation, hydrogen peroxide, interphase catalyst

**Synthesis and Characterization of Cr(III), Fe(III) and
Co(II) Complexes of 2,3,13,14-Tetra(ethyl/*p*-tolyl)-
-1,4,12,15-tetraazacyclodocosa-1,3,12,14-tetraene**

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**The Effect of 2,2'-Bipyridyne (1,10-Phenanthroline)
on the Stability of Co(II), Ni(II) and Cu(II)
Complexes with Acetic, Methoxyacetic, Phenylacetic
and Cyclohexylacetic Acids**

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